

Methanol adsorption on graphene

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The adsorption energies and orientation of methanol on graphene are determined from first-principles density functional calculations. We employ the well-tested vdW-DF method that seamlessly includes dispersion interactions with all of the more close-ranged interactions that result in bonds like the covalent and hydrogen bonds. The adsorption of a single methanol molecule and small methanol clusters on graphene are studied at various coverages. Adsorption in clusters or at high coverages (less than a monolayer) is found to be preferable, with the methanol C-O axis approximately parallel to the plane of graphene. The adsorption energies calculated with vdW-DF are compared with previous DFT-D and MP2-based calculations for single methanol adsorption on flakes of graphene (polycyclic aromatic hydrocarbons). For the high coverage adsorption energies we also find reasonably good agreement with previous desorption measurements.

I. INTRODUCTION

Methanol (CH_3OH) is the simplest of the alcohols, and it is used, e.g., as a solvent, an alternative fuel, and as a source for producing other chemicals. Methanol is the second most abundant organic molecule in the atmosphere next after methane (CH_4), and along with other insoluble aerosol particles methanol is believed to play a role in the formation of ice in the atmosphere, as discussed and modeled e.g. in Refs. [1, 2]. Methanol is also found in the interstellar medium, as methanol ice dust grains. The graphite surface is a suitable model for dust in the interstellar medium for such studies [3, 4].

In this paper we calculate by first-principles density functional theory (DFT) the adsorption energy of methanol on graphite at various degrees of coverage (less than one molecular monolayer), and we determine the distance from and the optimal angle of the methanol molecule C-O axis with the plane of graphene. For the DFT calculations we use the method vdW-DF [5, 6].

Previously, the adsorption energies of methanol from graphene or flakes of graphene were calculated [7] by the semi-empirical theory method DFT-D [8]. In the study of Ref. [7] the adsorption of methanol on to very small flakes of graphene—benzene and coronene—was also calculated by the higher-accuracy correlation method second-order Møller-Plesset perturbation theory (MP2). Desorption energies from highly oriented pyrolytic graphite (HOPG) or from various sizes of single-walled carbon nanotubes (SWCNTs) have also previously been measured in a number of desorption experiments [3, 9, 10].

The purpose of this study is to determine basic information about adsorbed methanol on graphene, such as the optimal orientation, the interaction (adsorption) energy at various coverages and distances from graphene, and to make these available as input to and/or for fine-tuning of molecular dynamics simulations of the methanol adsorption process.

In the following, we first introduce the methanol-graphene system, the vdW-DF method, and the set up of our calculations. Next, we describe our results both at low and high coverage of methanol on graphene and then discuss the relation to the theory results of Ref. [7] and some of the available experimental results.

II. MATERIALS AND METHODS

On some surfaces methanol chemisorbs. When this is the case, traditional semilocal DFT methods, based on the generalized gradient expansion (GGA), may suffice for describing the adsorption. For instance, this is the case on the oxide surfaces $\alpha\text{-Al}_2\text{O}_3(0001)$ and $\alpha\text{-Cr}_2\text{O}_3(0001)$ on which we previously studied methanol adsorption [11, 12]. However, on graphene a number of small molecules physisorb, or at least owe a significant part of their adsorption energy to the dispersion interaction. Then GGA methods are inadequate.

We here use the vdW-DF method [5, 6]. It includes the van der Waals (vdW) interactions (also termed the London dispersion interactions), that are especially important on intermediate to long ranges, along with all the traits of GGA for short-range interactions. Thus, vdW-DF delivers a description of the system that takes care of both the vdW interaction between the fragments (and within the fragments) and the short-ranged interaction within the molecules, like the covalent bonding, hydrogen bonding, possible ionic interactions etc., all from first principles.

Over the past few years, our group has carried out a series of physisorption studies of relatively small molecules on graphene: n-alkanes (of length 1 to 10 C atoms) [13], phenol [14], small polycyclic aromatic hydrocarbons (PAHs) [15, 16], trihalomethanes [17], adenine [18], and with somewhat different computational details, all of the five nucleobases of DNA and RNA [19]. General considerations of use of the vdW-DF method for such systems, as well as further method discussions, can be found in the Refs. [13–18] mentioned above.

We here use the DFT program GPAW [20] with a fast-

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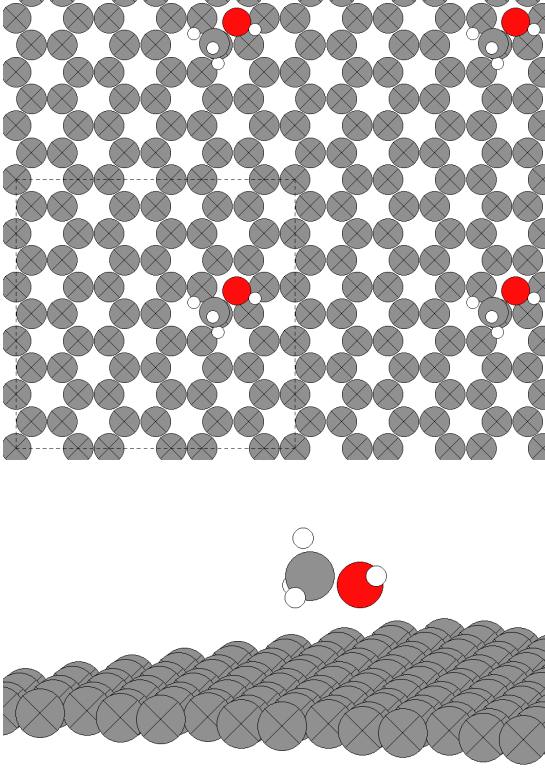


FIG. 1: Schematic view of a single methanol molecule adsorbed on graphene in the $3\sqrt{3}a_g \times 5a_g \times 19$ Å periodically repeated unit cell. The configuration with the C-O axis approximately parallel with graphene is shown. Gray circles with a cross are graphene C atoms. Other gray/red/small white circles are the methanol C, O and H atoms. In the top panel the unit cell is outlined by thin broken lines.

Fourier-transform implementation of vdW-DF [5, 6, 21]. Pre- and postprocessing is carried out in the python environment ASE [22].

We use periodic orthorhombic unit cells as detailed in Table I, with 8–60 graphene C-atoms per unit cell. The unit cell side lengths in the plane of graphene range from 4.29 to 12.87 Å with one, three or five methanol molecules per unit cell, as illustrated for one molecule in Figure 1 and for three and five molecules in Figure 2.

The wave functions are sampled on a regular grid with points 0.12 Å apart (the charge density is sampled at points half that distance apart) to obtain sufficient accuracy for high-quality results from the vdW-DF calculations [13, 23]. The reciprocal space k -point sampling is $2 \times 2 \times 1$ for the largest and $6 \times 8 \times 1$ for the smallest unit cell, except for the calculation of isolated methanol where only the Γ -point is used.

In all calculations the atomic positions are allowed to relax. We use the molecular-dynamics optimization method “fast inertial relaxation engine” (FIRE) [24] and require that the remaining force on each atom has a size of less than 0.01 eV/Å.

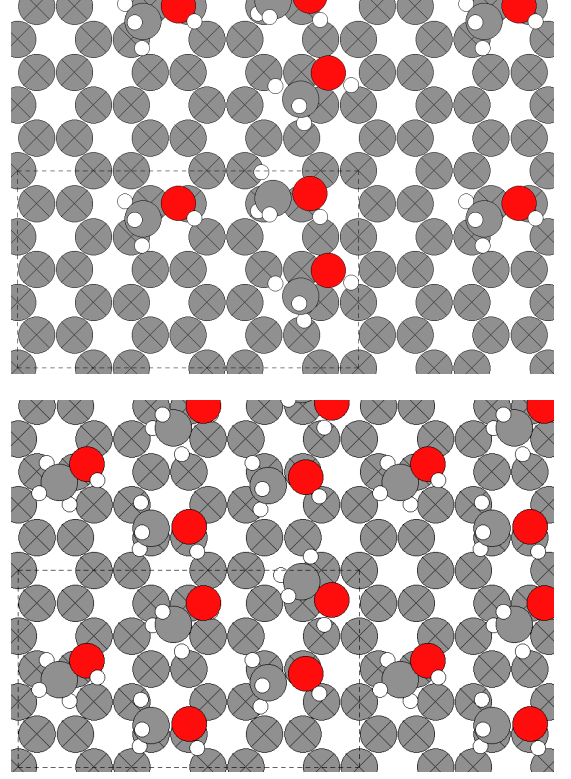


FIG. 2: Three- and five-molecule clusters in the $3\sqrt{3}a_g \times 3a_g \times 19$ Å unit cell.

We determine the adsorption energy E_a as the difference in total energies of the full system $E_{\text{tot,MeOH on graphene}}^{\text{vdW-DF}}$ and each fragment isolated,

$$E_a = E_{\text{tot,MeOH on graphene}}^{\text{vdW-DF}} - E_{\text{tot,graphene}}^{\text{vdW-DF}} - E_{\text{tot,MeOH}}^{\text{vdW-DF}}. \quad (1)$$

Here the first two terms are found using the unit cell size of the full system (Table I), whereas the last term is calculated in a $3\sqrt{3}a_g \times 5a_g \times 19$ Å unit cell with only Γ -point sampling. For the three- or five-molecule cluster calculations, equation (1) is changed appropriately to give the adsorption energy E_a per adsorbate (in eV) or per mol (in kJ).

The data points of the potential energy-curve in Figure 3 are obtained with a slightly longer unit cell than the other calculations: because we need to calculate the methanol-graphene interaction at up to relatively large separations (11 Å) the unit cell height is increased to 23 Å, all other settings remaining the same.

III. RESULTS AND DISCUSSION

In Table I we list the adsorption energies E_a for the various methanol-graphene systems that we consider. Also shown for each calculation is the coverage of methanol on

TABLE I: Theory data for adsorption of methanol on graphene. Included is the adsorption energy E_a , the distance of the methanol O atom from graphene, d_O , the adsorption configuration (C-O axis approximately parallel with the plane of graphene, or C-O axis approximately perpendicular to the plane of graphene with the O atom pointing up or down), molecular coverage, and the orthogonal unit cell used in the calculations, given in units of $a_g = \sqrt{3}a_0$ with $a_0 = 1.43$ Å. All unit cells are 19 Å in the direction perpendicular to the plane of graphene. The coverages in our calculations are estimated from the approximate molecular area of methanol on graphene 17.6 Å² determined from x-ray diffraction studies in Ref. [25].

	Structure	Unit cell	Coverage [ML]	E_a [kJ/mol]	E_a [meV]	d_O [Å]
<i>Theory, vdW-DF (our calculations)</i>						
single molecule	parallel	$3\sqrt{3} \times 5$	0.11	20.6	214	3.33
	parallel	$3\sqrt{3} \times 4$	0.14	20.7	215	3.33
	parallel	$3\sqrt{3} \times 3$	0.18	21.1	219	3.33
	O down	$3\sqrt{3} \times 3$	0.18	14.6	151	3.20
	O up	$3\sqrt{3} \times 3$	0.18	15.5	160	4.87
	parallel	$1\sqrt{3} \times 2$	0.83	30.5	316	3.55
three-cluster	parallel	$3\sqrt{3} \times 3$	0.55	30.4	315	3.31–3.54
five-cluster	parallel	$3\sqrt{3} \times 3$	0.92	34.9	361	3.35–4.50
<i>Theory, DFT-D and MP2-based (Pankewitz and Kloppe)^a</i>						
single molecule, DFT-D with BP86	parallel	benzene		14.8		3.35
single molecule, DFT-D with BP86	parallel	coronene		18.7		3.32
single molecule, DFT-D with BP86	parallel	112-C PAH		20.0		3.32
single molecule, DFT-D with BP86 ^b	O up	coronene		~11		~4.8
single molecule, SCS-MP2 with PB86	parallel	benzene		13.8		~3.4
single molecule, SCS-MP2 with PB86	parallel	coronene		18.3		~3.3

^aOrbital-based calculations with a TZVP basis, Ref. [7].

^bEnergy estimated from Figure 8 of Ref. [7].

graphene in units of molecular monolayers (ML), derived from the estimated area per molecule 17.6 Å² at 1 ML obtained by Morishige et al. [25] from x-ray diffraction studies of a methanol film on graphite.

In the $3\sqrt{3}a_g \times 3a_g$ unit cell we test starting the calculations with methanol oriented such that the C-O axis is either parallel or perpendicular to graphene (with the O atom pointing away from or towards graphene). As evident from Table I, the almost-parallel orientation, after relaxation of the atomic positions, is energetically more favorable than the two perpendicular orientations (“O up” and “O down”). While the parallel orientation gives rise to a 219 meV (21.1 kJ/mol) binding, the perpendicular orientations only bind with 160 and 151 meV (15.5 and 14.6 kJ/mol). For the remaining calculations we therefore start methanol oriented parallel to graphene.¹

Ignoring the E_a of the two perpendicular orientations (“O up” and “O down”) we see that E_a grows with increasing coverage, from 214 meV at 0.11 ML to 361 meV at 0.92 ML, the exception being the single molecule in the $1\sqrt{3}a_g \times 2a_g$ unit cell. We also find that the methanol-graphene distance, here measured as the distance to O in

methanol, d_O , slightly increases with coverage, although the trend is not clear for the cluster calculations.

As seen by the growth in E_a with coverage, the methanol molecules interact attractively, across unit cell boundaries (due to periodic boundary conditions) and for the cluster calculations also within the unit cell. The nearest-neighbor adsorbate-adsorbate distance in our single-molecule calculations varies from 12.4 Å in the largest unit cell to 4.3 Å in the smallest unit cell. In the cluster calculations the O-to-O nearest-neighbor separation is 3.0 Å in the three-adsorbate cluster (one such interaction per unit cell) and 2.9 Å in the five-adsorbate cluster (two such nearest neighbors per unit cell).

It should be noted that the cluster calculations are started with methanol distributed at “reasonable” inter-molecular separations, not specifically in any expected cluster-configuration, and the relative orientations are not optimized for the orientations at e.g. a full ML [25].

It is possible to partition the adsorption energy into the contributions from the substrate-adsorbate interaction and the adsorbate-adsorbate interaction. The adsorbate-adsorbate interaction energy is found from the total energy of the system with the graphene substrate removed, all other atom positions unchanged, and subtracting the total energy of an isolated molecule (times three or five for the clusters).

For the $3\sqrt{3}a_g \times 4a_g$ unit cell this attractive interac-

¹ We did check starting with the “O down” orientation in the small $1\sqrt{3}a_g \times 2a_g$ unit cell, but after full relaxation of the atomic positions methanol ended up with an orientation parallel to graphene.

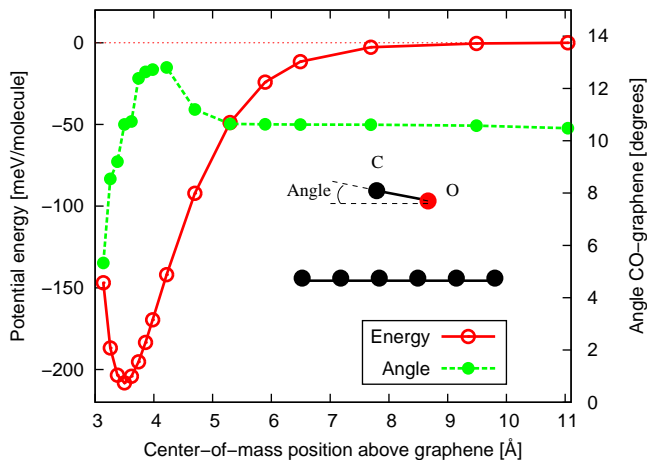


FIG. 3: Potential energy of a single molecules of methanol on graphene at various distances from graphene (open circles, left graph axis). In each calculated point of the curve the atoms of the methanol molecule are allowed to relax according to the forces on the atoms, with the constraint that the center-of-mass position is fixed. The angle that the C-O axis makes with the graphene plane is shown in the curve with solid circles (right graph axis). The insert defines the angle.

tion across cell boundaries amounts to a mere 2 meV per molecule (0.2 kJ/mol), increases to 7 meV (0.7 kJ/mol) for the $3\sqrt{3}a_g \times 3a_g$ unit cell, and 125 meV (12.1 kJ/mol) for the much more dense phase in the $1\sqrt{3}a_g \times 2a_g$ unit cell. For the three-cluster system the sum of adsorbate-adsorbate interactions per unit cell is 366 meV, thus in average 122 meV per molecule (11.8 kJ/mol). However, as noted above and seen also in the top panel of Figure 2, one pair of molecules per unit cell is closer together than the other pair interactions, and this pair interaction is thus expected to dominate the sum of interaction energies. This explains why the three-cluster system yields an adsorbate-adsorbate energy at only 0.55 ML that is almost the same as the evenly distributed molecules in the $1\sqrt{3}a_g \times 2a_g$ unit cell at 0.83 ML.

In the five-cluster calculations, the adsorbates are in reality almost uniformly distributed within the unit cell, and can hardly be considered a “cluster”. The coverage is close to a full ML and all molecules are relatively close to each other, although two O-O separations stand out as being smaller. We find the sum of adsorbate-adsorbate interactions per unit cell 909 meV, which yields an average 182 meV per adsorbate (17.5 kJ/mol), which is the largest adsorbate-adsorbate interaction energy of this study.

Thus the methanol-methanol interactions are important as they contribute a large fraction of the adsorption energy, but the methanol-graphene interaction is stronger. As discussed e.g. in Ref. [3] this facilitates the formation of a full methanol monolayer prior to forming multilayers, because the energy gain for the methanol

molecule is larger when binding to graphene than to other methanol molecules.

In Figure 3 the potential-energy curve of various graphene-methanol separations is shown. In this figure, each data point (circle) is found by keeping the center of mass of methanol relative to the plane of graphene at the distance d_{cm} , shown on the bottom axis of the figure. The atoms of the molecule are allowed to move in all directions, as long as d_{cm} remains unchanged. Thus, the orientation of the C-O axis changes with distance from graphene, as shown by the filled circles of Figure 3. When methanol is squeezed close to graphene ($d_{cm} \approx 3.2$ Å) the angle is smallest (the orientation is closest to being parallel), as a way for methanol to “avoid” a too close contact to graphene of any of its atoms. At the adsorption distance, the angle is approximately 10.6° . As the fragments are further separated, the angle grows a bit until the distance $d_{cm} \approx 5$ Å where the vdW interaction is too weak to change the angle from the initial angle 10.6° (each calculation is started with methanol in the adsorption configuration, translated towards or away from graphene).

Pankewitz and Kloppe [7] carried out non-periodic DFT-D calculations of methanol adsorbed on SWCNTs and PAH-models of graphene of size from benzene up to a PAH with 112 C atoms. Although the DFT-D calculations are semi-empirical and thus can be less accurate (depending on the choice of empirical parameters for each type of calculation) the adsorption energies on PAH (Table I) agree reasonably with the present results, when the smaller substrate size in the DFT-D calculations (due to lack of periodicity) is taken into account [18, 26]. For adsorption on to benzene and the PAH coronene (24 C) they also carried out spin-component scaled MP2 (SCS-MP2). Their SCS-MP2 result for methanol on coronene is in good agreement with the present results: From the DFT-D calculations we can estimate that approximately 1.3 kJ/mol of the methanol-substrate interaction is missing on coronene compared to graphene, or a rather large (112-C) PAH molecule. Their SCS-MP2 coronene result of 18.3 kJ/mol should therefore probably be corrected to ~ 19.6 kJ/mol for a single methanol molecule adsorption on graphene. For our largest unit cell we find 20.6 kJ/mol and less than a 0.1 kJ/mol correction for the periodicity. Thus our calculated energy for single methanol molecule adsorption deviates less than 1 kJ/mol (or 5%) from the estimate of the size-modified SCS-MP2 results. The distance of methanol O from graphene, d_O , turns out identical in the two calculations.

Interestingly, in the DFT-D calculations Pankewitz and Kloppe find a second, much weaker local minimum with the methanol O atom pointing away from coronene, much like our “O-up” configuration. For this configuration the energies and substrate-to-O distances are very similar, with 15.1 kJ/mol at 4.83 Å in the vdW-DF calculations and approximately 11 kJ/mol at 4.8 Å in the DFT-D calculations. In the binding energy curve of Figure 3 we do see a change in methanol angle with graphene

as the distance is varied, but at the 4.5–5 Å center-of-mass distance from graphene the interactions are probably too weak for the computational relaxation procedure to rotate the initially almost-parallel molecule to obtain the O-up structure.

Although we did no effort in fitting a full monolayer of methanol on to graphene, it is still of interest to compare our high-coverage results with other calculations of closely packed methanol molecules. Boyd and Boyd [27] used DFT with B3LYP at various basis set levels to calculate the binding energies and structures of (free-floating) methanol clusters of up to 14 molecules. They expect the inter-molecular interaction to be dominated by the hydrogen bonds, for which B3LYP behaves reasonably. They find the binding energy in the optimal clusters to be 27 kJ/mol, which is larger than our largest molecule-molecule energy 17.5 kJ/mol (for the 5-molecule cluster), but then, in our calculations there is still room for more molecules, and the molecules are constrained by the adsorption to graphene to form interactions only in two dimensions. Our smallest O-O distance of 2.9 Å (in the five-molecule cluster) compares well with the optimal O-O distance 2.77 Å in the trimer calculations of Ref. [27].

A number of experiments of methanol desorption from HOPG or SWCNTs have previously been carried out [3, 9, 10]. Although the desorption energies vary between the experiments, the energies for 1 ML coverage or less all fall in the range 28–51 kJ/mol (48 ± 3 kJ/mol at 1 ML [10], 33–48 kJ/mol at < 1 ML [3], 28 kJ/mol at < 1 ML [9]), with a tendency to increase with increasing coverage. The desorption energy range is in reasonable agreement with our results, that are in the range 20–35 kJ/mol (absent the less favorable methanol orien-

tations), with increasing adsorption energy for increasing coverage (Table I). None of the mentioned experiments measure the distance of methanol from the substrate, nor the orientation of methanol. Further comparison to experiments that are presently in progress will appear in a forthcoming publication [28].

IV. CONCLUSIONS

By use of the first-principles vdW-DF method we calculate adsorption energies and determine adsorption geometries of methanol on graphene. Our results are in reasonable agreement with other available calculations and experiments. This suggests that the data obtained here may be used as input parameters to or tests of results from calculations and models that (unlike DFT) rely on external information, either from experiment or from (preferentially) first-principles calculations. This could, for example, be models that are on larger length scales or with time dependency, such as molecular dynamics calculations.

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